I, Ikuzo Tanaka, Declare:

1. I am a citizen of Japan residing at 24-5, Mejirodai 4-chome, Hachiouji-shi, Tokyo, Japan.

2. To the best of my ability, I translated:

   **Japanese Patent Application No. 2001-012491**

   from Japanese into English and the attached document is a true and accurate English translation thereof.

3. I further declare that all statements made herein are true, and that all statements made on information and belief are believed to be true; and further that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Date: June 16, 2004          *Ikuzo Tanaka*
                             Ikuzo Tanaka

|  |  |  |
|---|---|---|
|  | **Document** | Application for Patent |
|  | **Ref. No.** | HO-0305 |
| 5 | **Filing Date** | January 19, 2001 |
|  | **To:** | Commissioner of The Patent Office |
|  | **IPC** | H01M   8/02 |
|  | **Inventor** |  |
|  | Address | c/o KABUSHIKI KAISHA HONDA GIJUTSU |
| 10 |  | KENKYUSHO |
|  |  | 4-1, Chuo 1-chome, Wako-shi, Saitama-ken |
|  | Name | Kaoru Fukuda |
|  | **Inventor** |  |
|  | Address | c/o KABUSHIKI KAISHA HONDA GIJUTSU |
| 15 |  | KENKYUSHO |
|  |  | 4-1, Chuo 1-chome, Wako-shi, Saitama-ken |
|  | Name | Keisuke Ando |
|  | **Inventor** |  |
|  | Address | c/o KABUSHIKI KAISHA HONDA GIJUTSU |
| 20 |  | KENKYUSHO |
|  |  | 4-1, Chuo 1-chome, Wako-shi, Saitama-ken |
|  | Name | Junji Matsuo |
|  | **Inventor** |  |
|  | Address | c/o KABUSHIKI KAISHA HONDA GIJUTSU |
| 25 |  | KENKYUSHO |
|  |  | 4-1, Chuo 1-chome, Wako-shi, Saitama-ken |

Name                Yuichiro Sugiyama

**Inventor**

Address             c/o KABUSHIKI KAISHA HONDA GIJUTSU

                    KENKYUSHO

5                   4-1, Chuo 1-chome, Wako-shi, Saitama-ken

Name                Nobuhiro Saito

**Applicant**

Registration No.    000005326

Name                HONDA GIKEN KOGYO KABUSHIKI KAISHA

10

**Agent**

Registration No.    100080012

Patent Attorney

Name                Kitsuma Takaishi

15    Tel           03(5228)6355

**Official Fee**

                    Paid in advance
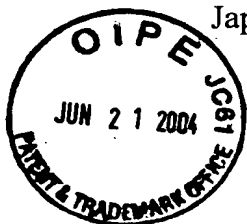
                    009324

                    21,000

20    **Attached Papers**

                    Specification              one

                    Drawings                   one

                    ABSTRACT                   one

**Necessity for Proof**         Yes

**SPECIFICATION**

**Title of the Invention**

POLYMER ELECTROLYTE FUEL CELL AND METHOD FOR PRODUCING
THEREOF

**Claims:**

1.          A polymer electrolyte fuel cell comprising a pair of opposing electrodes each having a catalytic layer and a polymer electrolyte membrane sandwiched by said electrodes, part of said catalytic layers being projecting into said polymer electrolyte membrane.

2.          The polymer electrolyte fuel cell according to claim 1, wherein the projection depth of said catalytic layer is 0.5 $\mu$m or more and less than 5 $\mu$m.

3.          The polymer electrolyte fuel cell according to claim 1 or 2, wherein when there are arbitrary two points, whose linear distance is 10 $\mu$m or more, in an interface of said polymer electrolyte membrane with each of said catalytic layers, the distance along said interface is longer than said linear distance by 15% or more on average.

4.          The polymer electrolyte fuel cell according to any one of claims 1 to 3, wherein the DC resistance of said polymer electrolyte membrane in a thickness direction determined by impedance measurement is 90% or less of the DC resistance of a membrane electrode assembly having the same structure except that part of catalytic layers do not project into a polymer electrolyte membrane.

5.          A method for producing a polymer electrolyte fuel cell by bonding catalytic layers of a pair of opposing electrodes to both surfaces of a polymer electrolyte membrane, comprising the steps of (1) coating a catalytic layer of one electrode with a solution of a polymer electrolyte in an organic solvent,

1

(2) coating and drying the resultant polymer electrolyte membrane with a catalyst slurry for the other electrode, while the amount of said organic solvent remaining in said polymer electrolyte membrane is 5-20 weight % based on said polymer electrolyte membrane, and (3) hot-pressing said

5    polymer electrolyte membrane in a state in which said polymer electrolyte membrane is sandwiched by both electrodes.

**DETAILD EXPLANATION OF THE INVENTION**

[0001]

**Field of the Invention**

The present invention relates to a polymer electrolyte fuel cell

5    capable of being subjected to low-humidifying operation and a method for

producing thereof.

[0002]

**Prior Art**

As the depletion of oil resources, global warming, etc. have been

10    becoming serious environmental problems, much attention has been paid to

fuel cells as clean power sources for motors, and wide development is now

carried out to put them in part into practical use.    Particularly when fuel cells

are mounted in automobiles, etc., they are preferably polymer electrolyte fuel

cells for the purpose of reduction in weight.

15    [0003]

In the polymer electrolyte fuel cell, a polymer electrolyte membrane

and both catalytic layers of electrodes should be moist to suppress decrease in

ion conductivity.    For this purpose, a fully humidified fuel is generally

supplied to a fuel electrode.    However, considering the miniaturization of a

20    fuel cell, it is preferable to put the fuel in a low or no humidification state.

[0004]

In the polymer electrolyte fuel cell, protons move with water

through the polymer electrolyte membrane from the fuel electrode to the

oxygen electrode.    Accordingly, the fuel electrode is likely to be dried,

25    resulting in likelihood of reduction in proton conductivity.    On the other

hand, if water is excessively generated in the oxygen electrode, a flooding

phenomenon (a phenomenon of closing the diffusion path of a gas by wetting

the catalytic layer) occurs by the electrode reaction.    Thus, water should be

supplemented in the fuel electrode, while water should be removed in the oxygen electrode.

[0005]

Proposed for such water control are (a) a method for humidifying a polymer electrolyte membrane via twisted threads embedded therein, or (b) a method in which a water absorbent is added to the electrodes (Japanese Patent Laid-Open No. 10-334922). However, the method (a) suffers from the problem that the polymer electrolyte membrane has a large thickness by sandwiching the threads, resulting in decrease in ion conductivity, and the method (b) suffers from the problem that the addition of the water absorbent lowers the ion exchange capacity of the electrodes.

[0006]

**Problems to be Solved by the Invention**

Accordingly, an object of the present invention is to provide a polymer electrolyte fuel cell capable of achieving low-humidifying operation without increasing a membrane thickness and decreasing an ion exchange capacity, etc., and a method for producing thereof.

[0007]

**Means for Solving the Problems**

As a result of intense research in view of the above objects, the inventors have found that in a polymer electrolyte fuel cell comprising electrodes having catalytic layers bonded to both surfaces of a polymer electrolyte membrane, a self-humidifying function can be obtained by causing the electrode catalytic layers to partially project into the polymer electrolyte membrane, thereby making it possible to carry out the low-humidifying operation of the polymer electrolyte fuel cell.

[0008]

Thus, the polymer electrolyte fuel cell of the present invention

comprises a pair of opposing electrodes each having a catalytic layer and a polymer electrolyte membrane sandwiched by the electrodes, part of the catalytic layers being projecting into the polymer electrolyte membrane.

[0009]

The projection depth of the catalytic layer is preferably 0.5 μm or more and less than 5 μm.    Also, when there are arbitrary two points, whose linear distance is 10 μm or more, in an interface of the polymer electrolyte membrane with each of the catalytic layers, the distance along the interface is preferably longer than the linear distance by 15% or more on average.

[0010]

The polymer electrolyte fuel cell having such a structure is desirably designed, such that the DC resistance of the polymer electrolyte membrane in a thickness direction determined by impedance measurement is 90% or less of the DC resistance of a membrane electrode assembly having the same structure except that part of catalytic layers do not project into a polymer electrolyte membrane.

[0011]

The method for producing a polymer electrolyte fuel cell comprising catalytic layers of a pair of opposing electrodes bonded to both surfaces of a polymer electrolyte membrane according to the present invention comprises the steps of (1) coating a catalytic layer of one electrode with a solution of a polymer electrolyte in an organic solvent, (2) coating and drying the resultant polymer electrolyte membrane with a catalyst slurry for the other electrode, while the amount of the organic solvent remaining in the polymer electrolyte membrane is 5-20 weight % based on the polymer electrolyte membrane, and (3) hot-pressing the polymer electrolyte membrane and the electrodes formed on both sides of the membrane.

[0012]

## Mode for Carrying Out the Invention

[1] Membrane electrode assembly

The polymer electrolyte fuel cell has a structure in which a plurality of membrane electrode assemblies generally shown in Fig. 1 are stacked via

5 separator plates. Each membrane electrode assembly is constituted by a polymer electrolyte membrane 1, and a fuel electrode 2 and an oxygen electrode 3 on both sides of the membrane 1, these members being sandwiched by separator plates 4, 4. The fuel electrode 2 and the oxygen electrode 3 are respectively constituted by diffusion layers 21, 31 and

10 catalytic layers 22, 32.

[0013]

(A) Polymer electrolyte membrane

The polymer electrolyte membrane of the present invention is made of a proton (ion) exchange resin, which may be not only sulfonated

15 perfluorocarbon, but also a sulfonated, non-fluorinated polymer such as sulfonated polyetheretherketone (PEEK), sulfonated phenoxybenzophenone-benzophenone copolymer, etc. Incidentally, an average thickness of the polymer electrolyte membrane is measured by a method shown in Fig. 2 below.

20 [0014]

(B) Electrode

The diffusion layers 21, 31 of respective electrodes (fuel electrode 2 and oxygen electrode 3) function not only to transmit electrons between the electrode catalytic layers 22, 32 and the separator plates 4, 4, but also to

25 diffuse a fuel gas (hydrogen) and an oxidizing gas (air) to the electrode catalytic layers 22, 32. Therefore, the diffusion layers 21, 31 should have both electric conductivity and porosity. Specifically, each diffusion layer 21, 31 preferably comprises a primary layer formed by coating a support layer

such as a carbon paper, a carbon cloth, a carbon felt, etc. with a slurry of conductive particles such as carbon black particles dispersed in an ion-conducting binder, which may be the same polymer electrolyte as above.

[0015]

Also, each catalytic layer 22, 32 is formed by coating each electrode diffusion layer 21, 31 with a catalyst slurry obtained by uniformly dispersing catalyst particles composed of platinum particles, etc. carried on carbon black particles in a solution of an ion-conducting binder in organic solvent.

[0016]

(C) Projection of catalytic layer

The feature of the present invention lies in that there are interfaces 11, 12 in a wave form between the polymer electrolyte membrane 1 and the electrode catalytic layers 22, 32 on both sides of the membrane 1 as shown in Fig. 2, whereby the electrode catalytic layers 22, 32 are partially projecting into the polymer electrolyte membrane 1. Because of the projection of the electrode catalytic layers 22, 32 into the polymer electrolyte membrane 1, the membrane electrode assembly exhibits not only a function inherent in an electrode catalyst, but also a function to generate water by the reaction of an oxygen gas and a hydrogen gas cross-leaking through the polymer electrolyte membrane 1. That is, because water formed by cross-leaking in the electrode /membrane interface under a low humidification condition and water formed by electrode reaction are efficiently diffused into the polymer electrolyte membrane 1, low-humidification operation is realized.

[0017]

The degree of projection of the catalytic layer into the polymer electrolyte membrane can be expressed by an average projection depth and an average interface length. Fig. 3 shows the average projection depth d of the catalytic layer 22 into the polymer electrolyte membrane 1. Interfaces 11

between the catalytic layer 22 and the polymer electrolyte membrane 1 are arbitrarily selected in the number of *n* or more (usually 7) to measure the difference between a top 11a and a bottom 11b in each interface 11, and the resultant differences are averaged to determine the average projection depth d.

5     In the present invention, the average projection depth d is preferably 0.5 μm or more and less than 5 μm.    When the average projection depth d is less than 0.5 μm, sufficient contact cannot be obtained between the catalytic layer and the polymer electrolyte membrane, resulting in insufficient cross-leaking, thus insufficient self-humidifying function.    On the other hand, when the

10    average projection depth d is 5 μm or more, excessive cross-leaking takes place.    The more preferred average projection depth d is 0.5-3 μm.

[0018]

Fig. 4 shows the length of an interface 11 between the polymer electrolyte membrane 1 and the catalytic layer 22.    The length of an interface

15    11 can be measured by a map meter, etc.    When there are arbitrary two points A, B, whose linear distance is 10 μm or more, in the interface 11, the distance between the two points A, B along the interface 11 (simply called "interface length") is longer than the linear distance by 15% or more on average.    The average interface length ratio (average ratio of interface length

20    / linear distance) is also obtained by averaging the interface length ratios at arbitrary *n* pairs of points (usually 7 pairs) or more.    When the average interface length ratio is less than 15%, the interface 11 has insufficient roughness, failing to achieve not only sufficient contact between the catalytic layer and the polymer electrolyte membrane but also sufficient cross-leaking.

25    [0019]

The degree of projection of the catalytic layers 22, 32 into the polymer electrolyte membrane 1 can be expressed by the DC resistance of the polymer electrolyte membrane 1. Because the DC resistance in a thickness

direction determined by the impedance measurement of the membrane electrode assembly is proportional to the average distance between the electrodes 2, 3, the fact that the DC resistance is small means that the degree of projection of the catalytic layers 22, 32 is large. When there is a large

5    degree of projection in the catalytic layers 22, 32, electrochemical distance between the electrodes is shortened by the projection effects of the catalytic layers 22, 32, while keeping strength and durability because the polymer electrolyte membrane 1 substantially maintains a physical average membrane thickness, thereby increasing the effect of reversely diffusing the generated

10    water in the polymer electrolyte membrane 1.

[0020]

In the present invention, assuming that the DC resistance of the membrane electrode assembly is $R_0$ when part of the catalytic layers 22, 32 are not projecting into the polymer electrolyte membrane 1, substantially

15    corresponding to the DC resistance of the polymer electrolyte membrane 1, the DC resistance R of the membrane electrode assembly when part of the catalytic layers 22, 32 are projecting into the polymer electrolyte membrane 1 is preferably 90% or less of $R_0$. When the DC resistance ratio (ratio of R /$R_0$) is more than 90%, the catalytic layers 22, 32 do not have sufficient

20    degree of projection, failing to achieve a self-humidifying function.

[0021]

Incidentally, because the catalytic layers 22, 32 are partially projecting into the electrolyte membrane 1 as shown in Fig. 2, the average membrane thickness t of the polymer electrolyte membrane 1 can be

25    determined by the following method. First, in a photograph showing the cross section of the membrane, a membrane thickness $t_a$ is measured at an arbitrary position a, and a membrane thickness $t_b$ is similarly measured at another position b. Such measurement is carried out at a large number of

(preferably 7 or more) positions to average the measured thickness values. The resultant average value is regarded as the average membrane thickness.

[0022]

(D) Separator plate

Each separator plate 4 is a metal plate provided with a large number of grooves 41 for gas passage at least one surface (usually both surfaces) not only for separating the membrane electrode assemblies, but also for serving as fixing members when the membrane electrode assemblies are stacked.

[0023]

[2] Method for producing membrane electrode assembly

(A) Formation of electrode

(1) Production of catalyst slurry

Taking a platinum catalyst as an example, the formation of the electrode is explained below. First, carbon black particles are caused to carry platinum particles to form catalyst particles. The resultant catalyst particles are uniformly dispersed in a solution of an ion-conducting binder, which may be the same as the above polymer electrolyte, in an organic solvent, to prepare a catalyst slurry. The organic solvents may be dimethyl acetamide (boiling point: 165.5°C), dimethylformamide (boiling point: 153°C), dimethyl sulfoxide (boiling point: 189°C), triethyl phosphate (boiling point: 115°C), N-methylpyrrolidone (boiling point: 202°C), etc. Incidentally, a weight ratio of catalyst particles / polymer electrolyte in the catalyst slurry is preferably 1/2-3/1.

[0024]

(2) Production of diffusion layer

A slurry comprising carbon black particles and particles of polytetrafluoroethylene (PTFE), etc. at a weight ratio of 1/3-5/1 uniformly dispersed in a solvent such as ethylene glycol, etc. is coated on one surface of

a support layer such as a carbon paper, etc., and dried to form a primary layer, thereby providing a diffusion layer constituted by the support layer and the primary layer. The thickness of the primary layer may be about 1-3 mg/cm$^2$.

[0025]

5    (3) Formation of catalytic layer

The catalyst slurry obtained in the above step (1) is coated on the primary layer of the diffusion layer in such an amount that the amount of platinum is 0.3-0.5 mg/cm$^2$ and dried, to produce a catalytic layer of the electrode.

10    [0026]

(B) Formation of polymer electrolyte membrane and lamination of electrode
      thereon

In the formation of the electrode catalytic layer on the polymer electrolyte membrane, the concentration of an organic solvent remaining in

15    the polymer electrolyte membrane should be 5-20 weight %. Accordingly, a solution of a polymer electrolyte in an organic solvent is applied to the catalytic layer of one electrode, and when the concentration of the organic solvent remaining in the polymer electrolyte membrane becomes 5-20 weight %, the catalyst slurry for the other electrode is applied to a surface of

20    the membrane, followed by bonding a diffusion layer for the other electrode thereto.

[0027]

Specifically, a solution of a polymer electrolyte in an organic solvent is first applied to the catalytic layer of one electrode. The amount of

25    an organic solvent remaining in the catalytic layer on one electrode is preferably about 5-20 weight %, more preferably about 5-15 weight %. Also, the concentration of the polymer electrolyte solution is in general preferably 5-30 weight %, more preferably 10-15 weight %. When the concentration of

the polymer electrolyte solution is less than 5 weight %, the projection depth of the catalytic layer is too large, and too much application is needed to achieve the desired membrane thickness.   On the other hand, when the concentration is more than 30 weight %, the polymer electrolyte solution has too high viscosity, resulting in difficulty in application.

[0028]

After drying the resultant polymer electrolyte membrane until the amount of the remaining organic solvent becomes 5-20 weight %, the membrane is coated with a catalyst slurry for the other electrode.   When the amount of an organic solvent remaining in the polymer electrolyte membrane is less than 5 weight %, the projection of the catalytic layer into the membrane is insufficient.   On the other hand, when it is more than 20 weight %, the projection depth of the catalytic layer is too large.   The preferred amount of the remaining organic solvent is 5-15 weight %.

[0029]

The catalyst slurry applied to the polymer electrolyte membrane preferably has as comparatively small a concentration of a solid component as 3-10 weight %.   When the solid component concentration of the catalyst slurry is less than 3 weight %, the catalytic layer has a too large projection depth.   On the other hand, when it exceeds 10 weight %, the projection of the catalytic layer is insufficient.

[0030]

The interface between the polymer electrolyte membrane and the catalytic layer can be provided with a desired wave form, by (a) adjusting the viscosity, the type of an organic solvent and the drying time, etc. of the catalyst slurry, (b) spraying an organic solvent onto the catalytic layer, or (c) adjusting the viscosity and casting pressure, etc. of the polymer electrolyte solution applied to the catalytic layer.

[0031]

(C) Hot pressing

After drying the catalyst layer, a diffusion layer for the other electrode is laminated and followed by hot-pressing.   The hot-pressing conditions are in general preferably a temperature of 60-200°C and a pressure of 1-10 MPa for 1-3 minutes.   Also, the hot-pressing may be carried out by dividing it in two times such that the first hot pressing conditions are at a temperature of about 60-100°C and under a pressure of about 1-10 MPa for about 1-3 minutes, and the second hot pressing conditions are at a temperature of about 120-200°C and under a pressure of about 1-10 MPa for about 1-3 minutes.

[0032]

**EXAMPLES**

The present invention will be described in detail referring to EXAMPLES below without intention of limiting the present invention thereto.

[0033]

EXAMPLE 1

(1) Production of catalyst slurry

Platinum particles were carried on carbon black (furnace black) particles at a platinum /carbon weight ratio of 1:1 to form catalyst particles. Separately, polyetheretherketone (available from Aldrich) was introduced into fuming sulfuric acid so that it was sulfonated to an ion exchange capacity (milli-equivalent of a sulfonic group per 1 g) of 2.4 meq/g, thereby obtaining sulfonated polyetheretherketone.   The sulfonated polyetheretherketone was dissolved in N-methylpyrrolidone (available from Aldrich) while refluxing, to form a sulfonated polyetheretherketone solution at a concentration of 12 weight %.   This sulfonated polyetheretherketone solution was mixed with

13

the catalyst particles to form a catalyst slurry at a weight ratio (catalyst particles/sulfonated polyetheretherketone) of 1:2.

[0034]

(2) Production of diffusion layer

A slurry comprising carbon black particles and polytetrafluoroethylene (PTFE) particles at a weight ratio of 1:1.5 uniformly dispersed in ethylene glycol was applied to one surface of a carbon paper, and dried to form a primary layer, thereby forming a diffusion layer constituted by the carbon paper and the primary layer.

[0035]

(3) Production of one electrode

The catalyst slurry obtained in the above step (1) was applied to the primary layer of the diffusion layer such that the amount of platinum was 0.3 mg/cm$^2$, dried at 60°C for 10 minutes and then vacuum-dried at 120°C, to form one electrode having a catalytic layer. The amount of the organic solvent remaining in this catalytic layer was 5.0 weight %.

[0036]

(4) Production of polymer electrolyte solution

The sulfonated polyetheretherketone obtained in the above step (1) was dissolved in N-methylpyrrolidone while refluxing, to form a polymer electrolyte solution having a viscosity of 7000 cps.

[0037]

(5) Production of membrane electrode assembly

The catalytic layer of one electrode obtained in the step (3) was coated with the polymer electrolyte solution obtained in the step (4) at an average dry membrane thickness of 50 μm. After drying until the concentration of the organic solvent remaining in the membrane reached 5.0 weight %, the catalyst slurry obtained in the step (1) was applied. The first

hot pressing was carried out under the conditions of 80°C, 5 MPa and 2 minutes, and then the second hot pressing was carried out under the conditions of 160°C, 4 MPa and 1 minute, to form a membrane electrode assembly.

5    [0038]

(6) Evaluation of properties

(a) Measurement of projection depth

According to the method shown in Fig. 3, the projection depth of the catalytic layer into the polymer electrolyte membrane was measured at 9

10   points, to determine an average projection depth from the measured values. The results are shown in Table 1.

[0039]

(b) Measurement of interface length

According to the method shown in Fig. 4, the length of an interface

15   between the catalytic layer and the polymer electrolyte membrane was measured at 9 points, to determine an average interface length from the measured values.    The results are shown in Table 1.

[0040]

(c) Measurement of DC resistance ratio

20   As shown in Fig. 5, the membrane electrode assembly constituted by the polymer electrolyte membrane 1 and a pair of electrodes 2, 3 was sandwiched by a pair of separator plates 4, 4 and then by current-collecting plates 6, 6, which were connected to an impedance analyzer 10.    After drying the polymer electrolyte membrane 1 by flowing a dry nitrogen gas

25   through both separator plates 4, 4, its DC resistance R in the membrane thickness direction was measured.    The membrane electrode assembly having no catalytic layer projection was also measured with respect to the DC resistance $R_0$ in a membrane thickness direction by the same method.    The

measured resistance values were used to determine a DC resistance ratio (R /R_0 ratio).    The results are shown in Table 1.

[0041]

(d) Measurement of cell resistance

5       An apparatus shown in Fig. 5 was used to generate electric power, with the air flowing through one electrode 4 and a pure hydrogen gas flowing through the other electrode 4.    The power generation conditions were a gas pressure of 100 kPa, a utility ratio of 50%, and a dew point of 80°C for both electrodes.    The cell pressure was atmospheric.    The humidification was

10    indirect humidification by a cathode gas.    The cell resistance ($\Omega/cm^2$) at a current density of 1 A/cm$^2$ was measured under these conditions.    The results are shown in Table 1.

[0042]

(e) Evaluation of power-generating performance

15    An apparatus shown in Fig. 5 was used to generate electric power, with the air flowing through one electrode 4 and a pure hydrogen gas flowing through the other electrode 4.    The power generation conditions were a gas pressure of 100 kPa, a utility ratio of 50%, and a dew point of 80°C for both electrodes.    The cell pressure was atmospheric.    The humidification was

20    indirect humidification by a cathode gas.    The cell voltage at a current density of 1 A/cm$^2$ was measured under these conditions.    The results are shown in Table 1.

[0043]

EXAMPLE 2

25    A membrane electrode assembly was produced under the same conditions as in EXAMPLE 1, except that the polymer electrolyte solution coated on the catalytic layer had a viscosity of 7000 cps, and that the catalyst slurry was applied after drying the polymer electrolyte membrane such that

the concentration of an organic solvent remaining therein was 10.6 weight %, and the resultant membrane electrode assembly was evaluated in the same manner as in EXAMPLE 1. The results are shown in Table 1 and Figs. 6-7.

[0044]

5    EXAMPLE 3

A membrane electrode assembly was produced under the same conditions as in EXAMPLE 1, except that the polymer electrolyte solution coated on the catalytic layer had a viscosity of 7000 cps, and that the catalyst slurry was applied after drying the polymer electrolyte membrane such that

10   the concentration of an organic solvent remaining therein was 14.4 weight %, and the resultant membrane electrode assembly was evaluated in the same manner as in EXAMPLE 1. The results are shown in Table 1 and Figs. 6-7.

[0045]

EXAMPLE 4

15   A membrane electrode assembly was produced under the same conditions as in EXAMPLE 1, except that the polymer electrolyte solution coated on the catalytic layer had a viscosity of 7000 cps, and that the catalyst slurry was applied after drying the polymer electrolyte membrane such that the concentration of an organic solvent remaining therein was 20.0 weight %,

20   and the resultant membrane electrode assembly was evaluated in the same manner as in EXAMPLE 1. The results are shown in Table 1 and Figs. 6-7.

[0046]

EXAMPLE 5

A membrane electrode assembly was produced under the same

25   conditions as in EXAMPLE 1, except that the polymer electrolyte solution coated on the catalytic layer had a viscosity of 7000 cps, and that the catalyst slurry was applied after drying the polymer electrolyte membrane such that the concentration of an organic solvent remaining therein was 10.6 weight %,

and the resultant membrane electrode assembly was evaluated in the same manner as in EXAMPLE 1. The results are shown in Table 1 and Figs. 6-7.

[0047]

EXAMPLE 6

5       A membrane electrode assembly was produced under the same conditions as in EXAMPLE 1, except that the polymer electrolyte solution coated on the catalytic layer had a viscosity of 7000 cps, and that the catalyst slurry was applied after drying the polymer electrolyte membrane such that the concentration of an organic solvent remaining therein was 10.6 weight %,

10   and the resultant membrane electrode assembly was evaluated in the same manner as in EXAMPLE 1. The results are shown in Table 1 and Figs. 6-7.

[0048]

EXAMPLE 7

A membrane electrode assembly was produced under the same

15   conditions as in EXAMPLE 1, except that the polymer electrolyte solution coated on the catalytic layer had a viscosity of 7000 cps, and that the catalyst slurry was applied after drying the polymer electrolyte membrane such that the concentration of an organic solvent remaining therein was 10.6 weight %, and the resultant membrane electrode assembly was evaluated in the same

20   manner as in EXAMPLE 1. The results are shown in Table 1 and Figs. 6-7.

[0049]

COMPARATIVE EXAMPLE 1

A membrane electrode assembly was produced under the same conditions as in EXAMPLE 1, except that the polymer electrolyte solution was

25   cast to form a polymer electrolyte membrane, and that after drying until the concentration of the remaining organic solvent reached 2.2 weight %, the catalyst slurry was coated on both surfaces of the membrane at a platinum amount of 0.3 mg/cm$^2$, and the resultant membrane electrode assembly was

evaluated in the same manner as in EXAMPLE 1.   The results are shown in Table 1 and Figs. 6-7.

[0050]

COMPARATIVE EXAMPLE 2

5   A membrane electrode assembly was produced under the same conditions as in EXAMPLE 1, except that the polymer electrolyte solution having a viscosity of 7000 cps was coated on the catalytic layer, and that after drying until the concentration of an organic solvent remaining in the polymer electrolyte membrane reached 4.1 weight %, the catalyst slurry was coated

10   thereon, and the resultant membrane electrode assembly was evaluated in the same manner as in EXAMPLE 1.   The results are shown in Table 1 and Figs. 6-7.

[0051]

COMPARATIVE EXAMPLE 3

15   A membrane electrode assembly was produced under the same conditions as in EXAMPLE 1, except that the catalyst slurry was sprayed onto the catalytic layer, and that after adjusting its surface roughness, a polymer electrolyte solution having a viscosity of 7000 cps was coated on this catalytic layer in such an amount that the resultant membrane had an average dry

20   membrane thickness of 50 $\mu$m, and that after drying until the concentration of an organic solvent remaining in the polymer electrolyte membrane reached 22.0 weight %, the catalyst slurry was coated thereon, and the resultant membrane electrode assembly was evaluated in the same manner as in EXAMPLE 1.   The results are shown in Table 1 and Figs. 6-7.

25

[0052]

Table 1

| No. | Membrane Thickness (μm) | Remaining Solvent (weight %) | Projection Depth (μm) | Interface Length (μm) | Average Interface Length Ratio |
|---|---|---|---|---|---|
| EXAMPLE 1 | 50 | 5.0 | 0.5 | 12.2 | 1.22 |
| EXAMPLE 2 | 50 | 10.6 | 1.2 | 12.0 | 1.2 |
| EXAMPLE 3 | 50 | 14.4 | 2.3 | 12.4 | 1.24 |
| EXAMPLE 4 | 50 | 20.0 | 3.0 | 12.2 | 1.22 |
| EXAMPLE 5 | 50 | 10.6 | 1.2 | 12.2 | 1.22 |
| EXAMPLE 6 | 50 | 10.6 | 1.2 | 13.0 | 1.3 |
| EXAMPLE 7 | 50 | 10.6 | 1.2 | 14.0 | 1.4 |
| COM. EX. 1 | 50 | 2.2 | 0 | 10.0 | 1.0 |
| COM. EX. 2 | 50 | 4.1 | 0.3 | 12.0 | 1.2 |
| COM. EX. 3 | 50 | 22.0 | 5.2 | 14.5 | 1.45 |

Table 1(continued)

| No. | Resistance R* | R/R₀** (%) | Cell Resistance ($\Omega/cm^2$) | Cell Voltage (V) |
|---|---|---|---|---|
| EXAMPLE 1 | 800 | 88.89 | 0.24 | 0.439 |
| EXAMPLE 2 | 717 | 79.67 | 0.18 | 0.442 |
| EXAMPLE 3 | 576 | 64.00 | 0.14 | 0.462 |
| EXAMPLE 4 | 300 | 33.33 | 0.12 | 0.458 |
| EXAMPLE 5 | 716 | 79.56 | 0.17 | 0.460 |
| EXAMPLE 6 | 718 | 79.78 | 0.18 | 0.463 |
| EXAMPLE 7 | 717 | 79.67 | 0.17 | 0.461 |
| COM. EX. 1 | 900 | 100.00 | 0.35 | 0.431 |
| COM. EX. 2 | 842 | 93.56 | 0.34 | 0.433 |
| COM. EX. 3 | 337 | 37.44 | 0.12 | 0.428 |

Note *:   Resistance in a dry state.

　　**:   $R_0 = 900 \ \Omega$.

5　　　　[0053]

　　　　Fig. 6 shows the relation between an average projection depth and a cell resistance and a power-generating performance (cell voltage).   When the average projection depth became 0.5 μm or more, drastic decrease in the cell resistance was observed.   However, at a time when the average projection

10　　depth exceeded 3 μm, the cell resistance became almost constant, indicating that influence by the average projection depth was saturated.   With respect to the power-generating performance, it reached a peak at an average projection

depth of around 2 μm, and its increase trend was reduced after exceeding that average projection depth.    This indicates that the average projection depth is preferably 0.5 μm or more and less than 5 μm, particularly 0.5-3 μm.

[0054]

5          Fig. 7 shows the relation between an average interface length ratio and a power-generating performance (cell voltage).    At the average interface length ratio of 1.15 or so, drastic decrease in the power-generating performance was observed.    When the average interface length ratio reached about 1.25, the effect of increasing the power-generating performance was

10      saturated.    This indicates that the average interface length ratio is preferably about 1.15 or more, particularly 1.15-1.25.

[0055]

          Fig. 8 shows the relation between a DC resistance ratio and a cell resistance.    When the DC resistance ratio became 90% or less, extremely

15      drastic decrease in the cell resistance was observed.    Also, when the DC resistance ratio reached about 50%, the effect of decreasing the cell resistance was saturated.    This indicates that the DC resistance ratio is preferably 90% or less.

[0056]

20      **Effect of the Invention**

          As described above in detail, because the polymer electrolyte fuel cell according to the present invention has a structure in which the catalytic layers on both sides project into the polymer electrolyte membrane, it exhibits excellent self-humidifying function.    Accordingly, low-humidifying

25      operation can be carried out without sacrificing a power-generating performance.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**Fig. 1:**    Fig. 1 is a schematic view showing the structure of a polymer electrolyte fuel cell according to the present invention;

**Fig. 2:**    Fig. 2 is a schematic cross-sectional view showing a state in which part of catalytic layers project into a polymer electrolyte membrane from both

5    sides in the polymer electrolyte fuel cell of the present invention;

**Fig. 3:**    Fig. 3 is a schematic cross-sectional view showing the projection depth of the catalytic layers into the polymer electrolyte membrane;

**Fig. 4:**    Fig. 4 is a schematic cross-sectional view showing the length of an interface between a catalytic layer and the polymer electrolyte membrane;

10    **Fig. 5:**    Fig. 5 is a schematic cross-sectional view showing an apparatus for measuring the impedance of the membrane electrode assembly;

**Fig. 6:**    Fig. 6 is a graph showing the relation between an average projection depth and a cell resistance and a power-generating performance (cell voltage);

**Fig. 7:**    Fig. 7 is a graph showing the relation between an average interface

15    length ratio and a power-generating performance (cell voltage); and

**Fig. 8:**    Fig. 8 is a graph showing the relation between a DC resistance ratio and a cell resistance.


**Descriptions of the Symbols**

20    1 · · · Polymer Electrolyte Membrane,

    11, 12 · · · Interface,

2 · · · Fuel Electrode,

    21 · · · Diffusion Layer of Fuel Electrode,

    22 · · · Catalytic Layer of Fuel Electrode,

25    3 · · · Oxygen Electrode,

    31 · · · Diffusion Layer of Oxygen Electrode, and
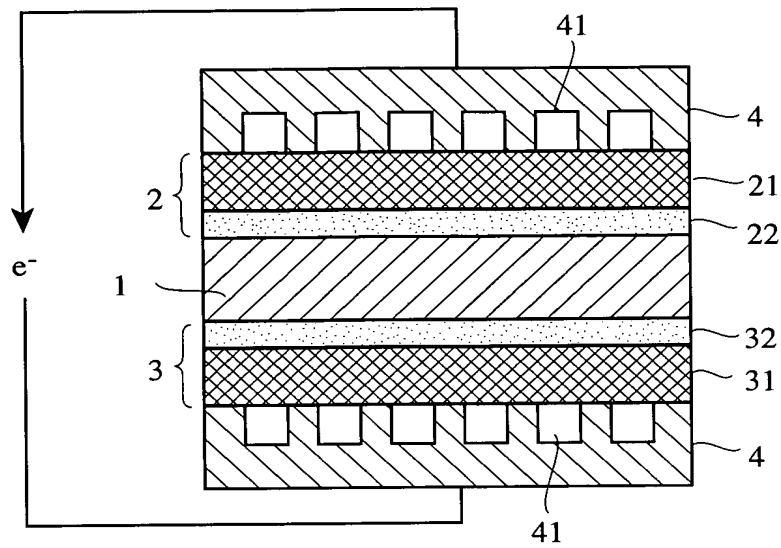
    32 · · · Catalytic Layer of Oxygen Electrode
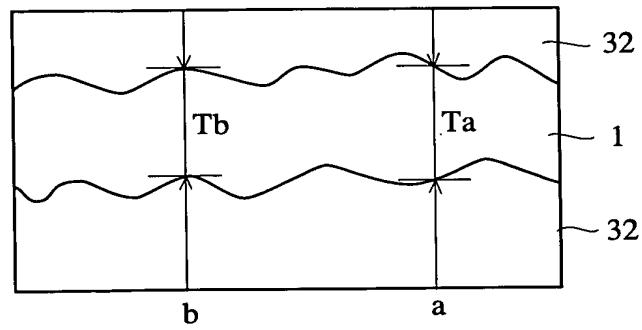
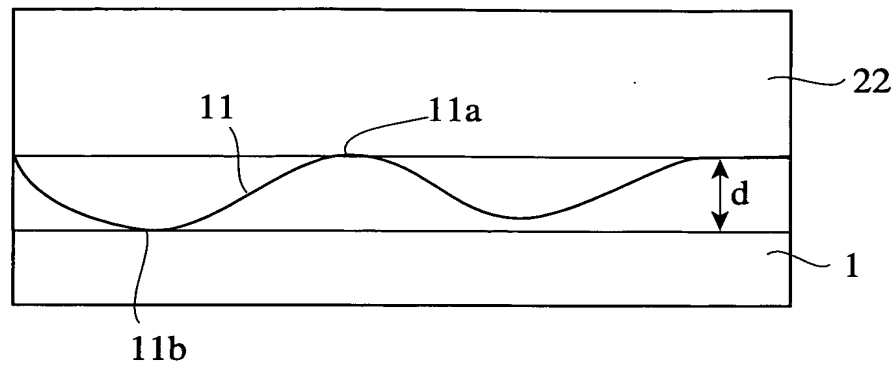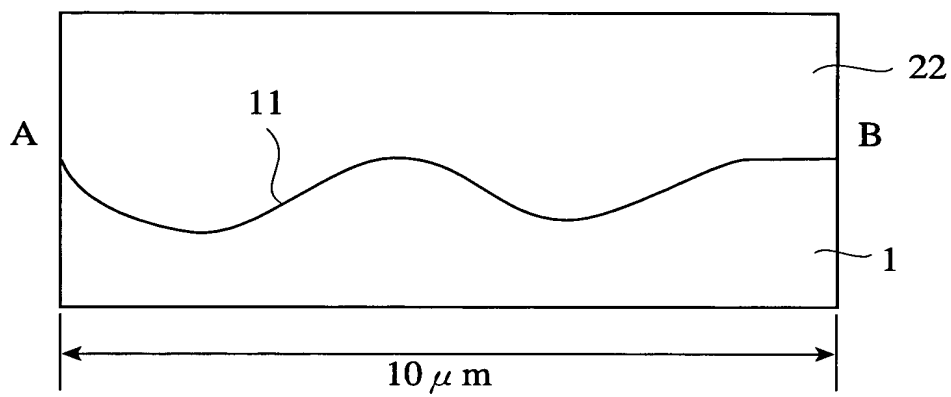# Fig. 1



# Fig. 2

# Fig. 3



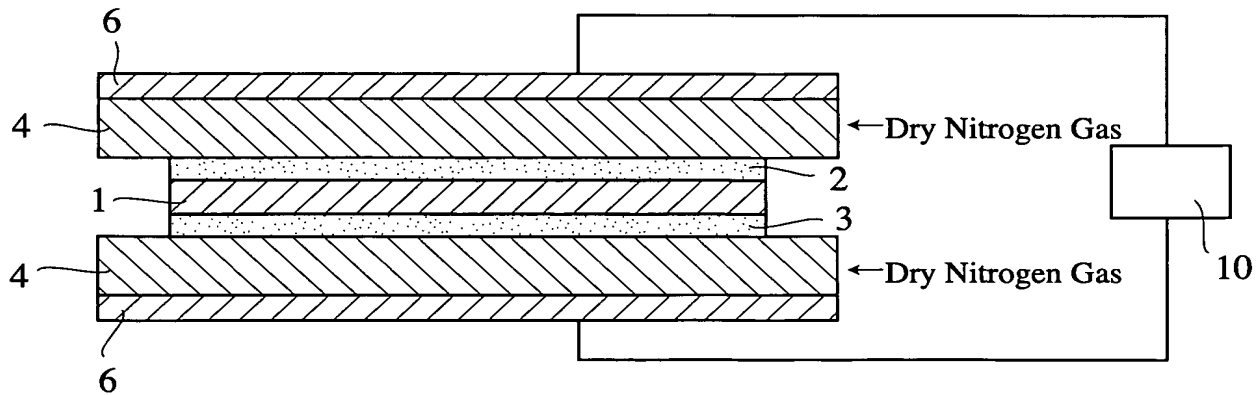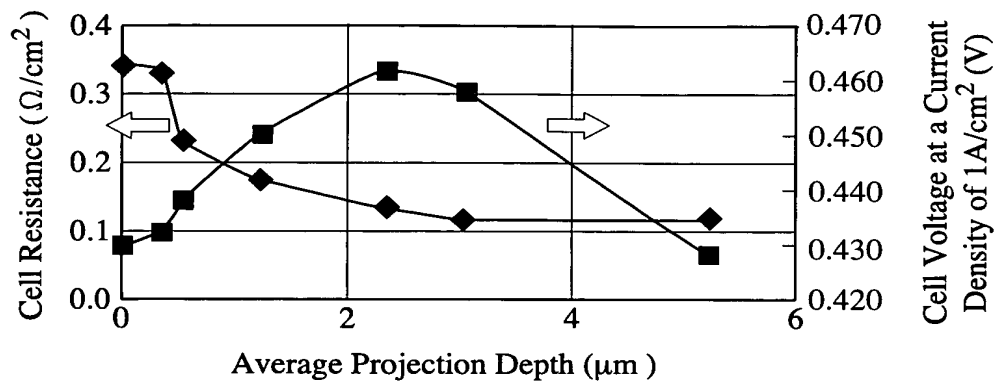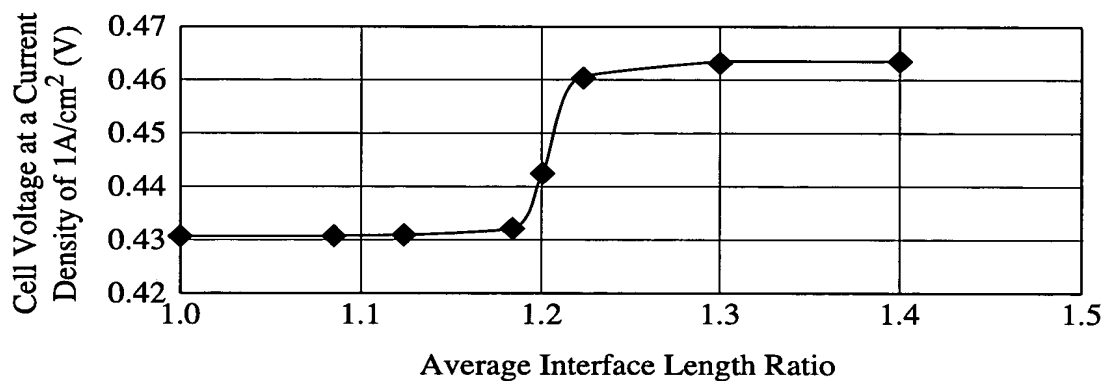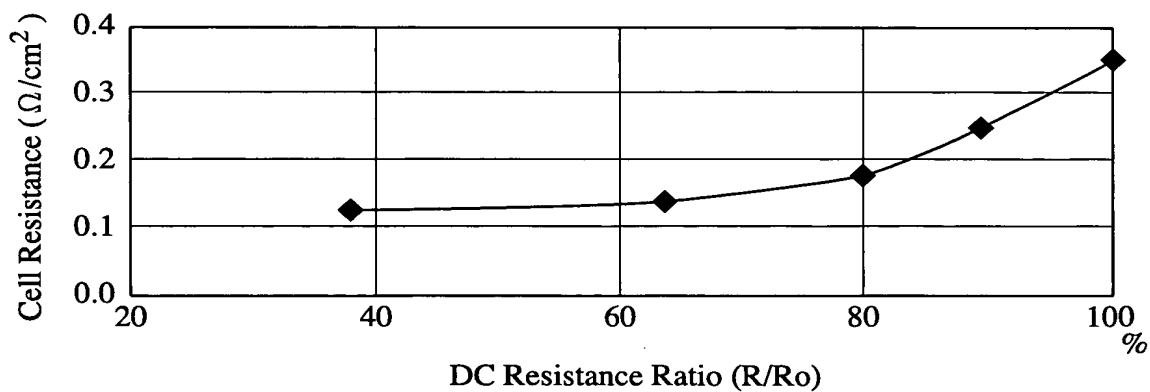# Fig. 4



# Fig. 5

# Fig. 6



# Fig. 7



# Fig. 8

## ABSTRACT

**Problems to be solved by the invention:**

To provide a polymer electrolyte fuel cell capable of achieving

5    low-humidifying operation without increasing a membrane thickness and

decreasing an ion exchange capacity, etc., and method for producing

thereof.

**Solution:**

A polymer electrolyte fuel cell comprises a pair of opposing

10    electrodes 2, 3 each having a catalytic layer 22, 32 and a polymer

electrolyte membrane 1 sandwiched by these electrode, the electrode

catalytic layers 22, 32 being partially projecting into the polymer

electrolyte membrane 1, wherein the polymer electrolyte fuel cell is

produced by (1) coating a catalytic layer 22 of one electrode 2 with a

15    solution of a polymer electrolyte in an organic solvent, (2) coating and

drying the resultant polymer electrolyte membrane 1 with a catalyst slurry

for the other electrode 3, while the amount of the organic solvent remaining

in the polymer electrolyte membrane is 5-20 weight % based on the

polymer electrolyte membrane, and (3) hot-pressing the polymer electrolyte

20    membrane 1 in a state in which said polymer electrolyte membrane 1 is

sandwiched by both electrodes 2, 3.

**Selected Drawings:**          Fig. 2